A Simple Acoustic Probe for Fluid Phase Equilibria: Application to the $CO_2 + N(C_2H_5)_3$ System

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Abstract

An acoustic technique was applied to investigate the critical behaviour of CO_2 + $N(C_2H_5)_3$. This study is part of a major programme on the determination of the critical behaviour of a series of tertiary amines in supercritical CO_2. Measurements of the critical temperature T_c and pressure p_c of the binary mixture of xCO_2 + $(1-x)N(C_2H_5)_3$ were performed restricted to the region richer in carbon dioxide, with x between 1 and 0.911. The Peng-Robinson equation of state with conventional mixing and combining rules, was used to correlate the binary experimental data. The course of the whole binary critical line was extrapolated. Additionally, this paper briefly reviews the experimental methods for determining critical properties. The theoretical basis of our acoustic method and the systems studied are discussed.

Keywords: Critical parameters, acoustic method, binary mixture, phase behaviour.

Introduction

In the current applications of supercritical fluids it is crucial to understand the phase behaviour of the multicomponent mixtures that are used in the chemical processes. Hence, the study of phase envelopes and critical points of complex mixtures is essential to optimise the operating conditions.

The critical parameters for pure thermally stable substances can be found in the literature however the data for multicomponent mixtures is very meagre. For ternary mixtures the available data are very scarce, even though the simplest reaction involves three substances.

Until the 1980s less than twenty ternary mixtures[1] had been reported.[2-13] This lack of information is related with the difficulty of applying to ternary mixtures the conventional visual methods of phase measurements. For these systems the density differences between the phases are usually small and therefore, the critical properties of ternary mixtures are often estimated by correlation methods [14-15] or by investigating the binary mixtures of their constituents and then predicting the properties of the ternary systems. Recently Sadus and Young [16-17] have measured the critical temperatures of some ternary mixtures.

The direct observation of the disappearance or reappearance of the meniscus is the most commonly used for the determination of the critical properties of pure fluids and multicomponent systems. This visual method is capable of reproducing critical temperature up to ± 0.1 K and critical pressure up to ± 0.2 MPa. [18] However, if the coexisting phases have a small density difference it would be very difficult to determine exactly the vanishing of the meniscus between the two phases and the measurement can

lead to substantial errors. The determination of the critical parameters using the acoustic technique described in this work overcomes this difficulty.

Although acoustic methods have been investigated since the end of the past century, it was only in the 1970s that were first reported the determinations of critical properties obtained by measuring the speed of sound near the critical point. [19-22] Most of these acoustic experiments have involved very high precision measurements, but only on pure substances. These experiments proved that acoustic measurements of the critical parameters for pure substances could be of the same precision as those obtained by the conventional methods. These apparatus used were generally quite bulky and the acoustic cell presented a specific geometry, usually a radial spherical symmetry, in order to obtain highly accurate measurements of the speed of sound. By contrast, the apparatus recently developed [23] has a very simple cell and no particular geometry is needed.

In this work, the acoustic method was used to investigate the critical behavior of $CO_2+N(C_2H_5)_3$. This study is part of a major programme on the determination of the critical behaviour of a series of tertiary amines in supercritical CO_2. Recent work has shown that supercritical media have very promising features for NMR spectroscopy. [24] Characterisation of compounds containing nitrogen and the acquisition of direct structural information about the coordination environment by means of ^{14}N and ^{15}N NMR are hindered by the quadrupolar moment of the ^{14}N isotope and by the low natural abundance of the ^{15}N isotope. The use of supercritical media, such as $scCO_2$, may partially alleviate the problem of quadrupolar line broadening. Once the fluid reaches its supercritical state the ^{14}N line width decreases appreciably. Evidence of this result has been recently reported by Gaemers et al. [25] The acoustic technique enables in a fast

and simple manner to define the critical boundary for the mixtures of carbon dioxide with coordination compounds containing quadrupolar nuclei of interest.

In this paper, the principle of our acoustic method applied to pure components and mixtures is described.

The binary mixture $CO_2 + N(C_2H_5)_3$ exhibits a pressure maximum. The course of the whole binary critical line was extrapolated using the Peng-Robinson equation of state with conventional mixing and combining rules.

Description of the Method

As it was mentioned, in conventional measurements of speed of sound, high precision acoustics apparatus are used. In contrast, our acoustic method does not require these accurate measurements, since the speed of sound is not measured directly. Instead, we measure the time of flight of an ultrasonic pulse. Changes in the transit time are inversely proportional to the speed of sound, and the maxima in the time of flight are used to determine the occurrence of phase transitions.

The basis of the experiment therefore consists of a cell in which an acoustic pulse can be delivered to the fluid and detected by a separate transducer. The source impulse is generated mechanically through a piezoelectric transducer. The transducers must be mounted into the cell body in such a way that they are physically separated, at a fixed distance, so that the acoustic signal cannot travel preferentially through the material of the cell body.

The acoustic method is capable of reproducing critical temperature up to $\pm$ 0.1 K and critical pressure up to $\pm$ 0.05 MPa. The applicability of this technique to pure substances is accurate and straightforward. The isothermal compressibility ($k_T = -1/V.(\partial V/\partial p)_T$) and the heat capacity at constant pressure of a fluid ($C_p = T.(\partial S/\partial T)_p$), are two well known

physical properties that diverge to infinity in the vicinity of the critical point of a pure substance. Some studies [26] developed by Bagatskii et al., Voronel et al. and by Edwards et al. strongly suggest that the specific heat at constant temperature ($C_v = T.(\partial S/\partial T)_v$), also becomes infinitive at the critical point, which is in disagreement with the classical van der Waals theory. However as pointed out by Levelt Sengers [27] the divergence of the C_v is weak compared to that of the k_T.

The critical point of the pure fluid is defined by the following conditions: [28]

$$(\partial p / \partial V)_T = 0 \tag{1}$$

$$(\partial^2 p / \partial V^2)_T = 0 \tag{2}$$

The sound velocity at zero frequency, c_o, of a pure component, can be expressed by the relation [29]:

$$c_o = [-V^2.(C_p/C_v)(\partial p/\partial V)_T]^{(1/2)} \tag{3}$$

The reason of using low frequencies in these measurements is related with the minimisation of the effects of vibrational relaxation, which occur at higher frequencies.

The combination of the tendency to zero of $(\partial p/\partial V)_T$ and (C_p/C_v) leads to the characteristic minimum of the sound velocity at the critical point to pure substances. So, by measuring the variation of the sound velocity in a fluid, the critical parameters can be obtained.

For mixtures, the conditions for the isothermal compressibility and the heat capacity at constant pressure divergence at a critical point are met only when an azeotrope persists up to the critical line.[30] In other cases, these two physical properties are finite. However, as Levelt Sengers [31] explains, if the critical point is approached from the one phase region, the isothermal compressibility may be seen to increase up to the critical point and reaches a local maximum. This result strongly suggests that this

method is also suitable for mixtures without an azeotropic behaviour. In our acoustic apparatus the critical point is approached from the liquid phase. Experiments are carried out at constant temperature and the pressure is lowered until a maximum in time delay is observed, meaning that it is reached a local maximum in the compressibility, corresponding to a phase transition. The temperature is then systematically varied and the procedure repeated. The temperature and pressure values corresponding to the absolute maximum of time delay in the ensemble of the isothermal curves is taken as the critical temperature and pressure.

In any case, the validation of this acoustic method for mixtures by comparison with binary critical lines measured by standard thermodynamics procedures should be presented and is reported here.

Pure components

In order to further evaluate the feasibility of the method and the accuracy of the apparatus, experimental critical data on CO_2, C_2H_6, CF_3CH_2F and Xe were reported [23,32] and compared with published values. For the measurement of critical data of each pure fluid several isotherms were measured in the vicinity of the critical temperature. The critical temperature and critical pressure of the pure components are in agreement with the literature values within the combined experimental errors.

Multicomponent systems

The accuracy of the acoustic technique when applied to study the critical behaviour of multicomponent systems was evaluated by comparing critical data obtained using the acoustic technique and other experimental methods. Acoustic measurements on the CO_2+CHF_3 system were performed on several mixtures covering the whole mole fraction range. [33] The comparison of the results obtained with those obtained by

Suehiro et al. [34] and Diefenbacher et al. [35] using the traditional visual methods is reported in a previous paper. [33] The acoustic results are in agreement with those obtained by the conventional methods, within the combined experimental errors.

Several other binary and ternary mixtures have been already investigated using the same acoustic technique, table 1 summarises the systems studied.

TABLE 1: Critical data of multicomponent mixtures obtained by acoustic measurements.

Systems	Reference
Binary Systems	
$CO + C_2H_4$	[37]
$CO + CH_3CHCH_2$	[37]
$CO_2 + Xe$	[32]
$CO_2 + CH_2F_2$	[37]
$CO_2 + CHF_3$	[33]
$CO_2 + CF_3CH_2F$	[23]
$CO_2 + N(C_2H_5)_3$	This work
$C_2H_6 + CHF_3$	[33]
$C_2H_6 + CF_3CH_2F$	[23]
$C_2H_4 + CH_3CHCH_2$	[37]
$CH_2F_2 + CF_3CH_2F$	[37]
Ternary Systems	
$CO_2 + CH_2F_2 + CF_3CH_2F$	[37]
$CO + C_2H_4 + CH_3CHCH_2$	[37]
$CO_2 + C_2H_6 + CHF_3$	[33]

For the binary systems containing CO, no literature data were available.

Supercritical mixtures of carbon dioxide and xenon might provide an environment for reactants and activated complex in a reaction that would be easily tuneable by changing the compositions of the solvent. [32] For this type of studies knowledge of the critical line in the phase diagram is essential. Moreover, the former information enabled to

extend to supercritical region the compelling evidence suggested by Calado and collaborators [36] that xenon behaves in fluid mixtures as if it was the first member of the n-alkane family.

Mixtures of CO_2 + fluorinated hydrocarbons are potentially attractive as modifiers for improving solubility in supercritical CO_2, thus three systems of CO_2 with refrigerants were studied [23,33,37] showing which refrigerants can be useful modifiers for supercritical

Although C_2H_6 and CO_2 are quite similar in their critical properties, mixtures of alkanes with partially or totally fluorinated alkanes were studied as its usually show a very different fluid phase behaviour from that of mixtures with CO_2.

As it was mentioned in the introduction, the determination of the ternary critical properties empirical correlations [14,38] or computational work, [16,39] are commonly used instead of experimental measurements. Furthermore, when experimental critical data are available for a certain system, there are typically only between one and four data points. [16]

Most of the ternary systems included in table 1 were investigated by a quasibinary approach, which means that the ratio of two of the three components was held constant.

The ternary systems CO_2 + CH_2F_2 + CF_3CH_2F [37] and CO_2 + C_2H_6 + CHF_3 [33] were studied as an extension of previous work on their binary subsystems.

The ternary system CO + C_2H_4 + CH_3CHCH_2 [37] is used for the production of aliphatic polyketone polymers. Although the knowledge of the critical surface is essential to improve the synthesis of these polymers, there were no data available in the literature.

Experimental Apparatus

A detailed description of the apparatus and the experimental procedure can be found in our earlier publication on CO_2 + Xe mixtures. [32]

Pressure was generated via a hand pump (High Pressure Equipment Co., Model 62-6-10) and monitored with a pressure transducer (Omega, Model PX931) with a precision of ± 0.01 MPa. Temperature was measured on the ITS-90 with a precision of ± 0.001 K with a calibrated platinum resistance thermometer (Tinsley) connected to a digital multimeter (Keithley, model 2000).

CO_2 was supplied by Ar Liquide with a purity greater than 99.99 per cent and $N(C_2H_5)_3$ was supplied by Aldrich with a purity greater than 99.5 per cent. The several mixtures were prepared in a stainless steal cylinder and the composition was measured by weighing. The accuracy of the composition is estimated to be ± 0.003 mole fraction.

Results and Discussion

Carbon dioxide with triethylamine is a model system to study the feasibility of ^{14}N NMR spectroscopy in supercritical fluids, which requires a detailed knowledge of the phase behaviour of the solvent.

The determination of the critical line of the $CO_2 + N(C_2H_5)_3$ system was restricted to the region near the critical point of pure carbon dioxide, with x_{CO_2} between 1 and 0.91 since the mixture critical temperature of this system is too high to investigate with our equipment. Six different isopleths were investigated and a representative set of data points for the isopleth $0.971\ CO_2 + 0.029\ N(C_2H_5)_3$ is shown in Figure 1, as a time delay-pressure diagram. As it was expected, the time delay increases when the mixture approaches the critical point.
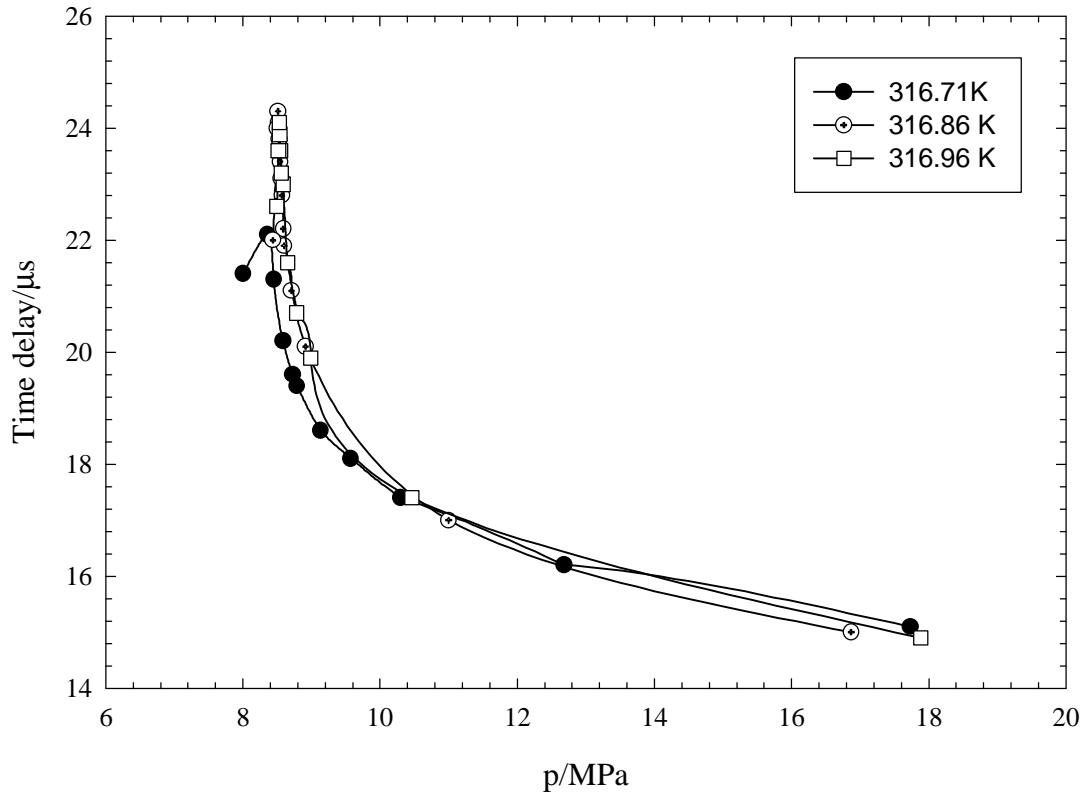
Figure 1. Near-critical isotherms for the mixture 0.971 CO_2 + 0.029 $N(C_2H_5)_3$. Some data points in the vicinity of the maxima were omitted for clarity. Subcritical isotherm is marked with filled black symbols, supercritical isotherm with outline symbols and the critical isotherm with a center dotted circle, for convenience of the reader experimental mark points are connected by a continuous line.

The experimental critical data obtained for the binary mixture are shown in Table 2. The estimated errors of the mixture critical parameters reported are 0.1 K for the critical temperature and 0.05 MPa for the critical pressure. The estimate was based on the comparison of the results of different experiments performed with the same mixture and is mainly determined by the narrowness of isotherms studied as during an experiment

the pressure decreases in a continuous way.

TABLE 2: Experimental critical data, p_c and T_c, of the binary system $CO_2 + N(C_2H_5)_3$.

x_{CO_2}	p_c/Mpa	T_c/K
0.989	7.66	307.18
0.982	7.99	310.85
0.975	8.37	315.17
0.971	8.51	316.86
0.961	8.65	319.60
0.911	10.3	335.98

The course of the whole binary critical line was extrapolated using the Peng-Robinson equation of state. [40] The pure fluid values used in PR EOS are presented in Table 3.

TABLE 3: Parameters of the pure substances used in the Peng-Robinson equation of state.

Component	p_c/MPa	T_c/K	ω_i
CO_2 [41]	7.38	304.2	0.239
$N(C_2H_5)_3$ [42]	3.03	535.0	0.320

The deviation parameters, k_{ij} and l_{ij}, were varied so that the theoretical critical line would give the best fit of the experimental results. Figure 2 shows the (p,T) projection of the critical line for this system using $k_{ij} = 0.12$ and $l_{ij} = 0.005$.
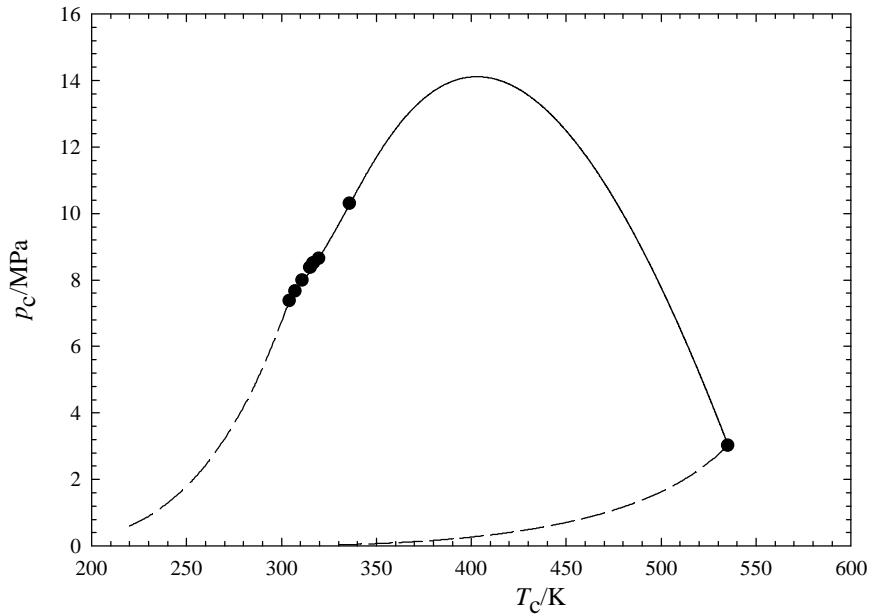
Figure 2. *p-T* projection of the binary critical curve of the system $CO_2 + N(C_2H_5)_3$. ($\bullet$) acoustic data; (——) predicted critical line using the PR EOS; (----) vapour pressure curves for pure components. [42]

The system exhibits type I fluid phase behaviour, according to the classification of van Konynenburg and Scott. [43] It can be seen that the system exhibits a large pressure maximum located at 401.7 K, 14.12 MPa and at $x(CO_2) = 0.78$. This behavior was expected since the critical curve of a binary mixture, with respect to composition, depends on the ratio of critical pressure to critical temperature of the pure components. [44] A similar behavior occurs in the methane + propane and methane + n-heptane systems. [45] When the pure component critical temperatures differ appreciably as in this case, the critical pressures increase rapidly with the amount of solute $(N(C_2H_5)_3)$ in the gaseous phase (CO_2).

Conclusion

Critical data of pure components and binary and ternary mixtures can be measured accurately using the acoustic technique described. The critical behaviour of carbon dioxide with triethylamine that is a model system to study the feasibility of ^{14}N NMR spectroscopy in supercritical fluids was investigated. Measurements of the critical temperature T_c and pressure p_c of this binary mixture of $xCO_2 + (1-x)N(C_2H_5)_3$ were performed restricted to the region richer in carbon dioxide, with x between 1 and 0.911. The predicted critical line, using the Peng-Robinson equation of state, connects the critical points of the two pure components and shows a distinctive pressure maximum. The determination of critical data of carbon dioxide with other amines is under study and will be subject of further publication.

Acknowledgement

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